Clean and Secure Energy from Coal

Contract Number: DE-NT0005015

Principal Investigator: Philip J. Smith, Director, Institute for Clean and Secure Energy

DOE support: $2,585,715

University of Utah Cost Share: $646,679

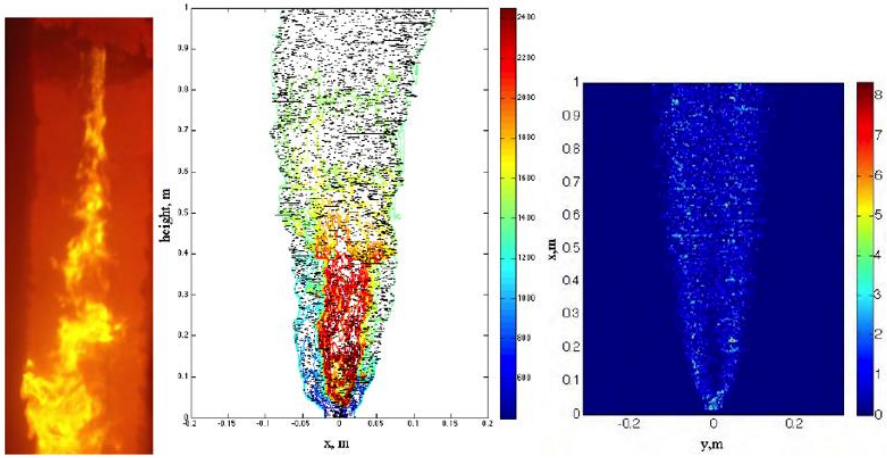
Total Support: $3,232,394

Contract Period: October 1, 2009 to March 31, 2011

Program Objectives

Major thrust is the use of complementary theoretical and experimental studies to provide simulation tools with error quantification, in order to reduce time to and risk in commercialization. The problems under study are:

- **The impact of CO_2 on flame stability, ash transformation, NOx and SOx emissions for both pulverized and fluidized bed oxyfuel combustion**
- **The entrained-flow gasification of coal with emphasis on coal pyrolyis, soot formation, char and soot burnout and slag/refractory interactions**
- **Chemical looping combustion for solid fuels with ASPEN system modeling and CFD detailed modeling**
- **Underground coal thermal treatment to gasify/liquefy coal in-situ with capture of CO_2 in the residual char**
- **CO_2 sequestration with experimental in-house studies of kinetics of CO_2 and SO_2 reactions with rock formations.**



The above technical activities are complemented by policy and legal studies assessing regulatory gaps in CCS.

Chemical Looping with Oxygen Uncoupling

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Institute for Clean and Secure Energy
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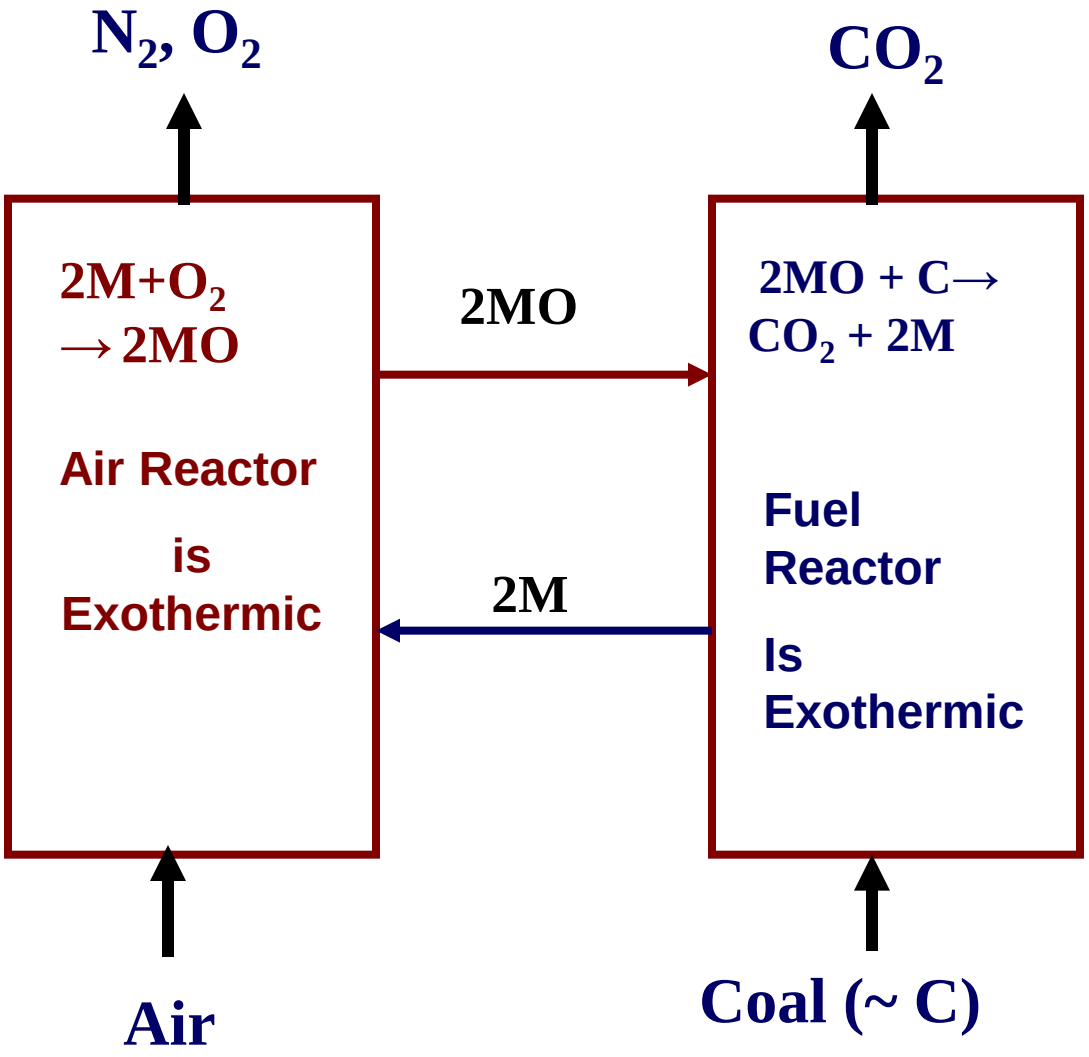
Salt Lake City

2010 NETL CO_2 Capture Technology Meeting
Sheraton Station Square, Pittsburgh, PA
September 15, 2010

Outline

- **Definition of Chemical Looping Combustion (CLC), its benefits, and differences between CLOU and CLC**
- **Oxygen Carrier Circulation Rate for CLOU**
- **Oxygen Carrier Loadings for CLOU**
  - **Kinetics of CuO decomposition and Cu_2O oxidation**
- **Carbon loading calculations**
- **Order of Magnitude Design Considerations**
- **Concluding Comments**
  - **Advantages of CLOU**
  - **Future Direction**

Chemical Looping Combustion



Air Reactor

$2M + O_2 = 2\,MO$ (Exo)

Fuel Reactor

oxidation occurs via a gasification reaction

$2MO + 2CO = 2CO_2 + 2M$

$C + CO_2 = 2\,CO$

$2\,MO + C = CO_2 + 2M$ (Endo)

Overall Reaction

$2M + O_2 = 2\,MO$ (Exo)

$2MO + C = CO_2 + 2M$ (Endo)

$C + O_2 = CO_2$ (Exo)

Energy is supplied to Fuel Reactor by circulating hot solids from Air Reactor

CLC is very successful with gaseous fuels (e.g., CH_4, CO, H_2). The challenge with solids is that reactions proceed via the slow gasification of $C + H_2O$ and $C + CO_2$.

Benefits of CLC

- **Estimates in Alstom Report, 2003**

Energy penalty for CLC versus reference atmospheric pressure FBC estimated to be 13%
Engineering procurement cost estimated to be $1663/kW for CLC with CO2 capture compared to US$1304/kW for Air fired CFB without CO2 capture, or an increase of 27.5%

- **Report by ENhanced CAPture of CO_2 (ENCAP), Ekstrom et al., 2009**

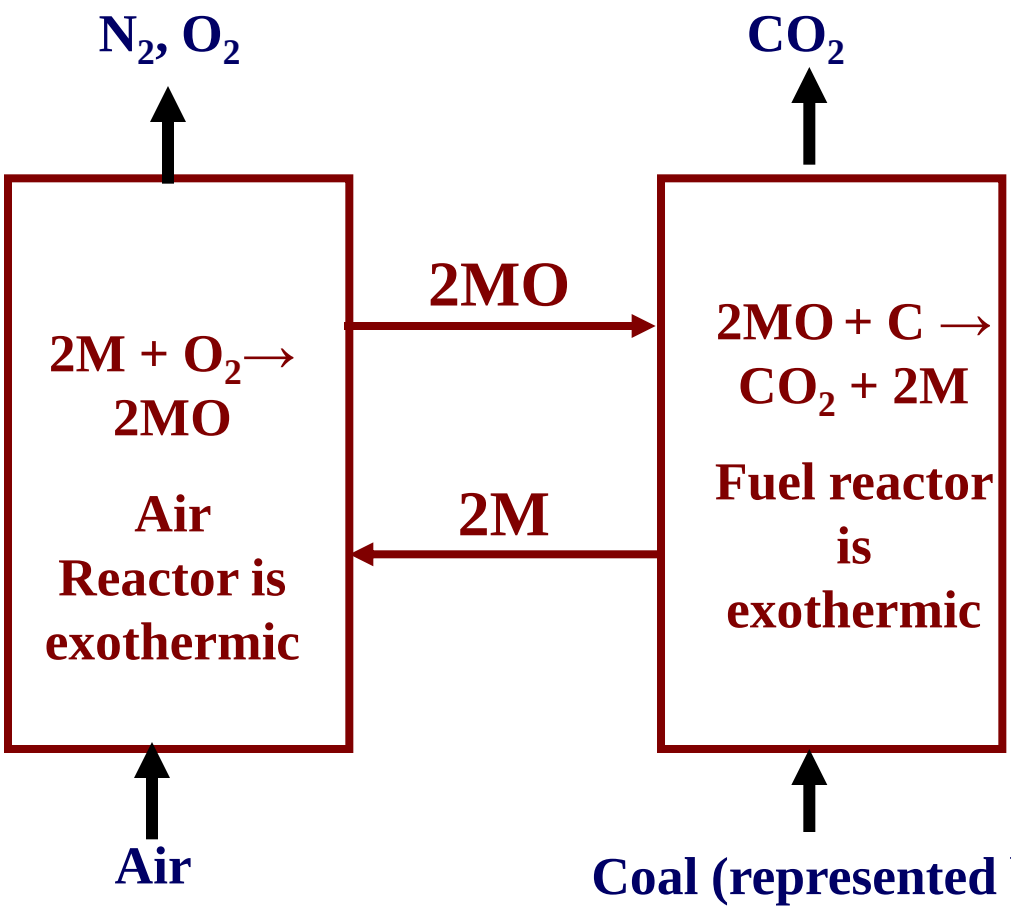
	Gross MWe	Net MWe
Ref. Case: Circulating Fluidized Bed (CFB), state of the art 2004, Bit. Coal	445	403
CLC CFB with same fuel flow and steam parameters as ref. case	455	387

~ 4% energy penalty and 13 to 22% increase in cost of electricity

CLC classified by ENCAP with the "More future" power plant concepts

Chemical Looping Combustion with Oxygen Uncoupling (CLOU)

Key Difference: The oxygen carrier dissociates at high temperature to yield oxygen for combustion reactions



Air Reactor

$2M + O_2 = 2\,MO$ (Exo)

Fuel Reactor

$2MO = 2M + O_2$ (Endo)

$C + O_2 = CO_2$ (Exo)

$2\,MO + C = CO_2 + 2M$ (Exo)

Overall Reaction

$2M + O_2 = 2\,MO$ (Exo)

$2MO + C = CO_2 + 2M$ (Exo)

$C + O_2 = CO_2$ (Exo)

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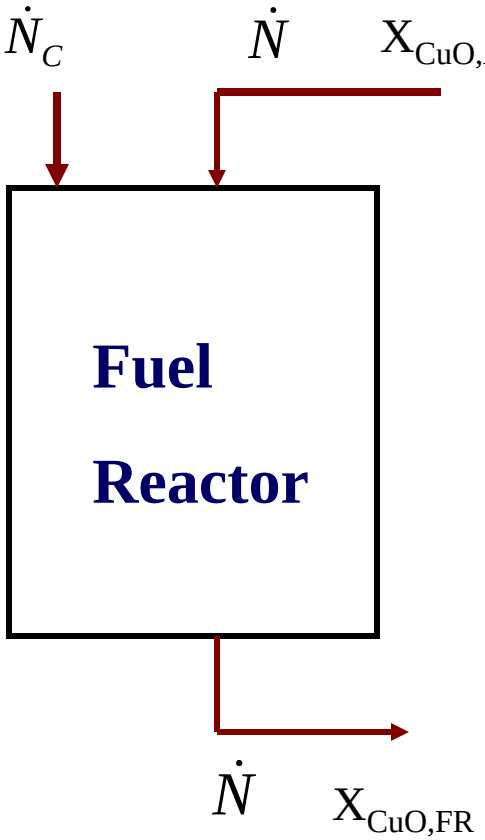
Major Advantage of CLOU over CLC

- **CLOU with a CuO oxygen carrier has been found to produce burnout times of petroleum cokes shorter than those for CLC with iron-based carriers by factors of 50 (Mattisson, 2009) and 60 (Lewis, 1951).**

- **Following sections will show the importance of this increase in rate to determining the amount of oxygen carrier needed.**

Calculation of Mass Circulation Rate



Let

$\dot{N}$ *be the mole flow rate of Cu circulating*

$\dot{N}_C$ *be the moles of carbon feed*

$$X_{CuO} = \frac{\dot{N}_{CuO}}{\dot{N}_{CuO} + 2\dot{N}_{Cu_2O}} = \text{mole fraction of Cu in form of CuO}$$

$$\dot{N}_C = \dot{N}_{O_2} = \left(\dot{N}_{CuO,AR} - \dot{N}_{CuO,FR}\right)/4$$

$$\left(\text{from } 4CuO + C \rightarrow 2Cu_2O + CO_2\right)$$

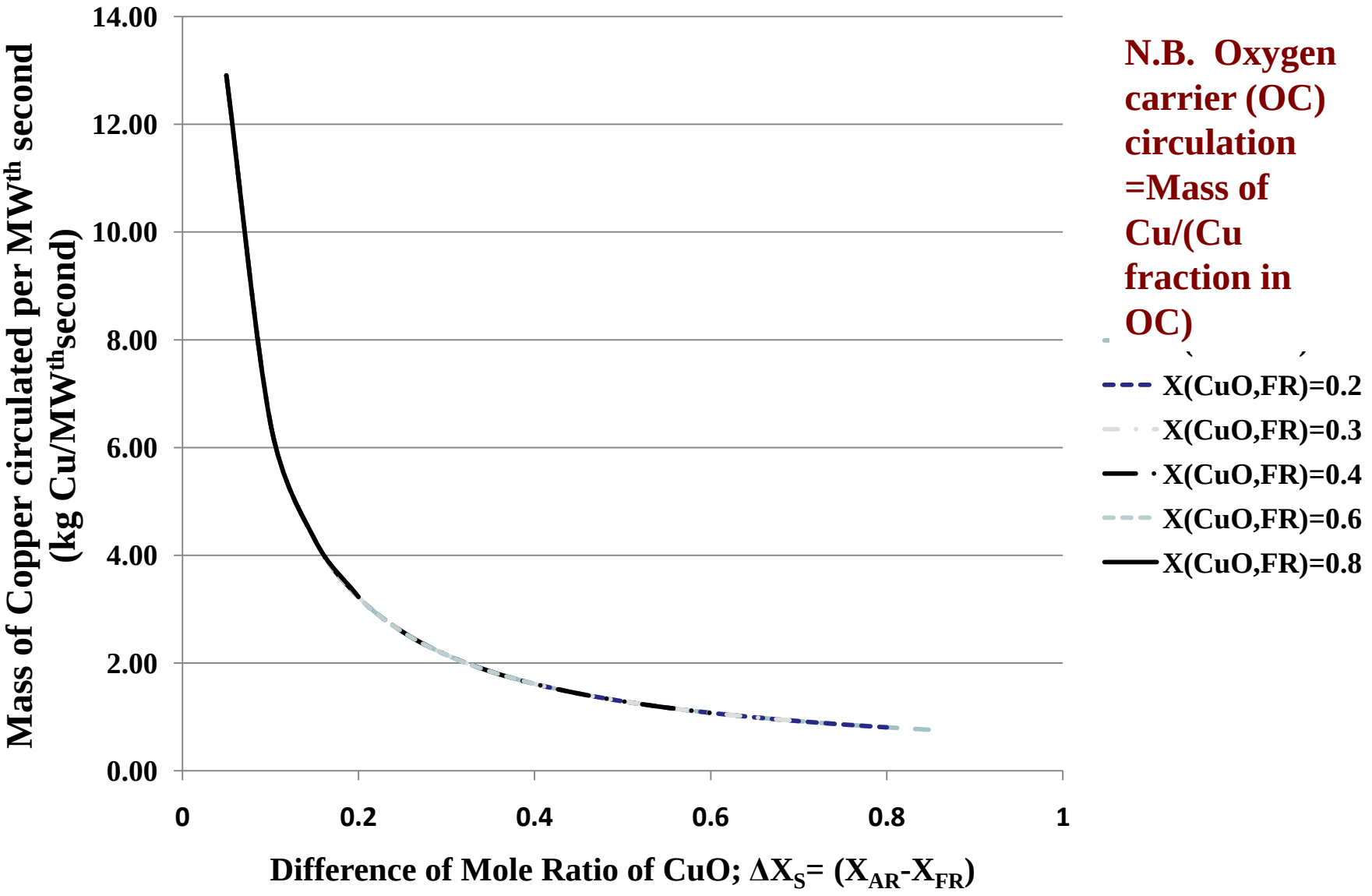
$$\Rightarrow \text{Dividing by } \dot{N}$$

$$\dot{N}_C = \dot{N}\left(X_{CuO,AR} - X_{CuO,FR}\right)/4$$

$$\dot{N}_C = \dot{N}\left(X_{CuO,AR} - X_{CuO,FR}\right)/4$$

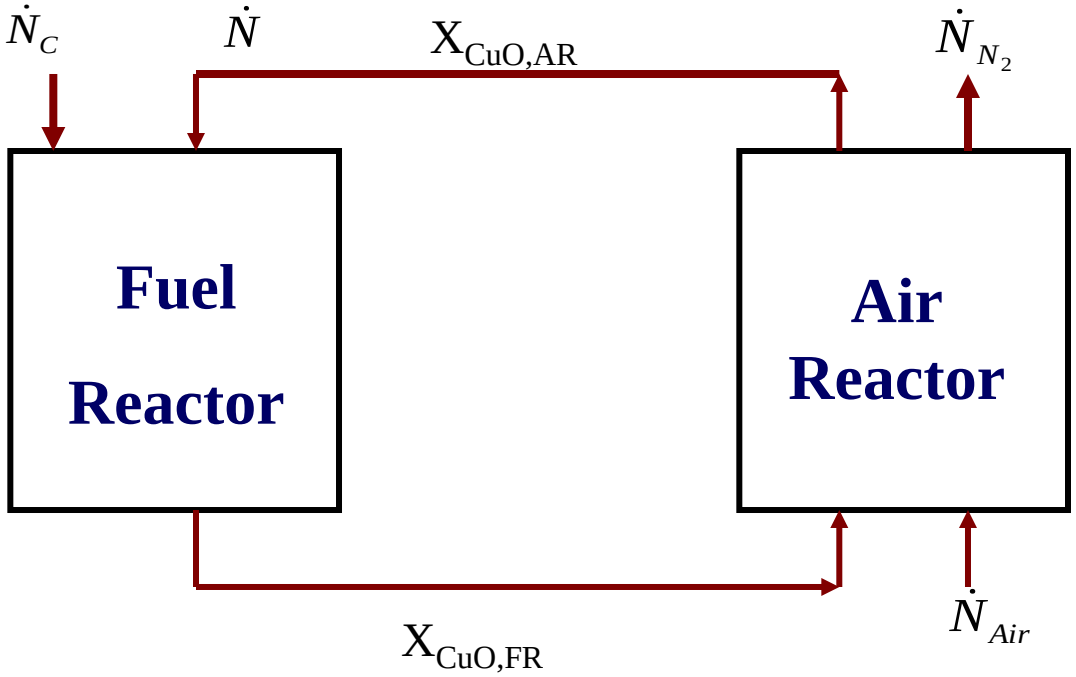
$$\frac{\dot{N}}{\dot{N}_C} = \frac{4}{\left(X_{CuO,AR} - X_{CuO,FR}\right)}$$

Plot of Mass of Copper circulated per MW^{th} second vs. Difference of Mole Ratio of CuO



Oxygen Carrier Loading

Oxygen Carrier Loading



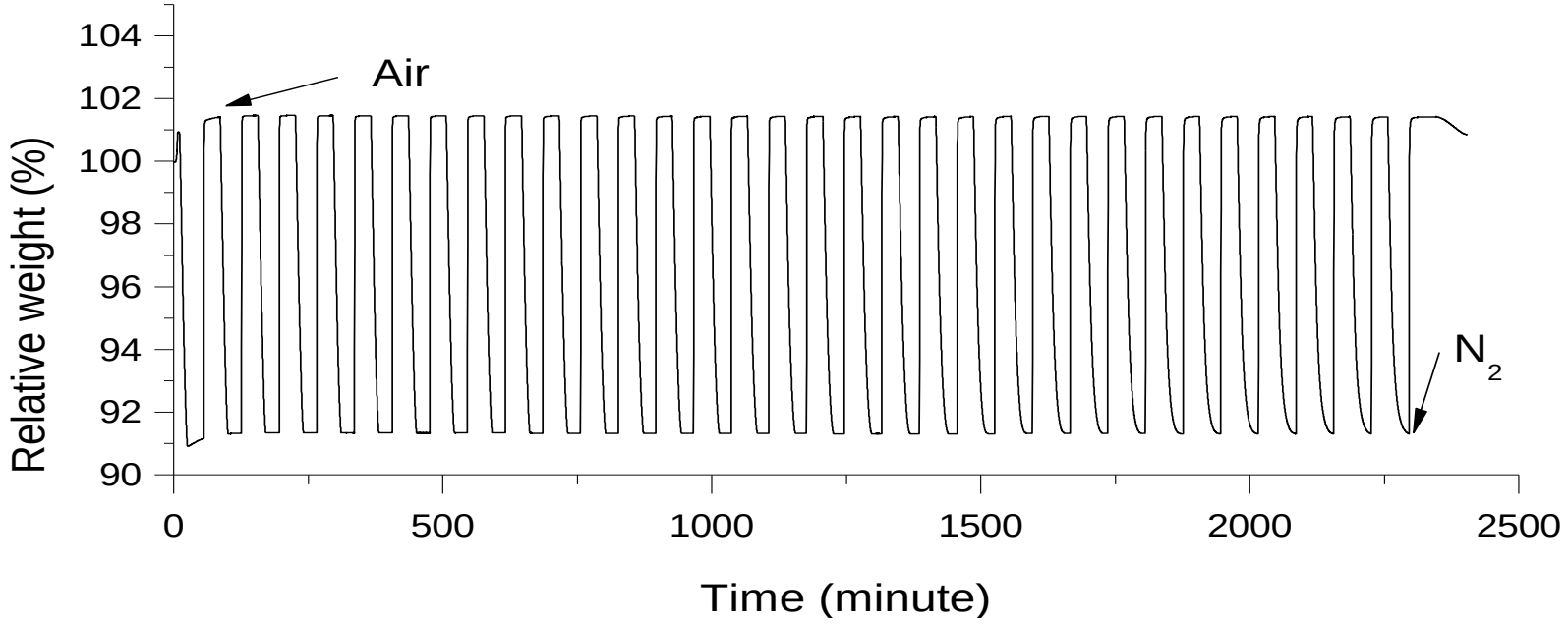
The mole copper loadings of oxygen carrier in the fuel and air reactors are equal to the circulation flow rate $\dot{N}$ times the residence times of the carrier in each reactor. The residence times are controlled by:

- The time needed to oxidize the Cu_2O in the air reactor
- The time in the fuel reactor which is controlled by the larger of 1. the time to burnout the char, 2. the time to decompose the CuO.

The kinetics of the conversion of Cu_2O to CuO, the reverse reaction, and the ability to cycle the reaction have been studied. The preliminary studies are for unsupported oxides.

CuO/Cu_2O Kinetics

Cycling atmosphere to TGA between air (30 min) and nitrogen (40 min) at 850 C to determine stability of CuO as an oxygen carrier.



Results suggest that CuO decomposes to Cu_2O based on weight loss (~10%)

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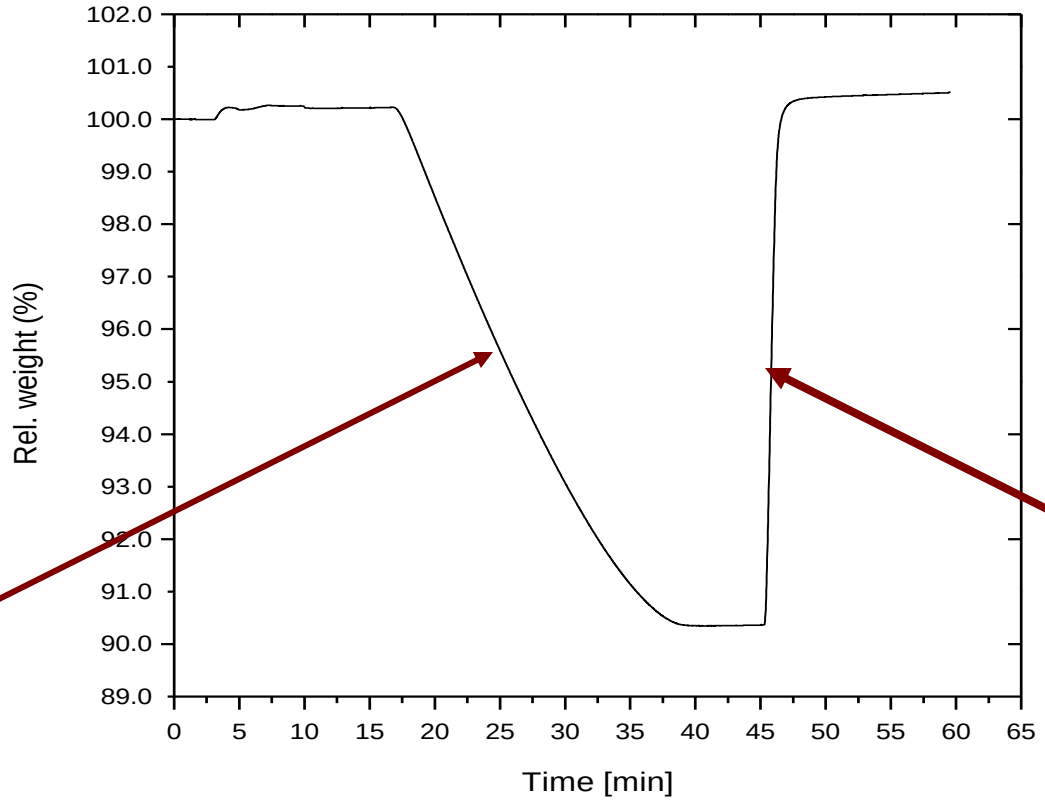
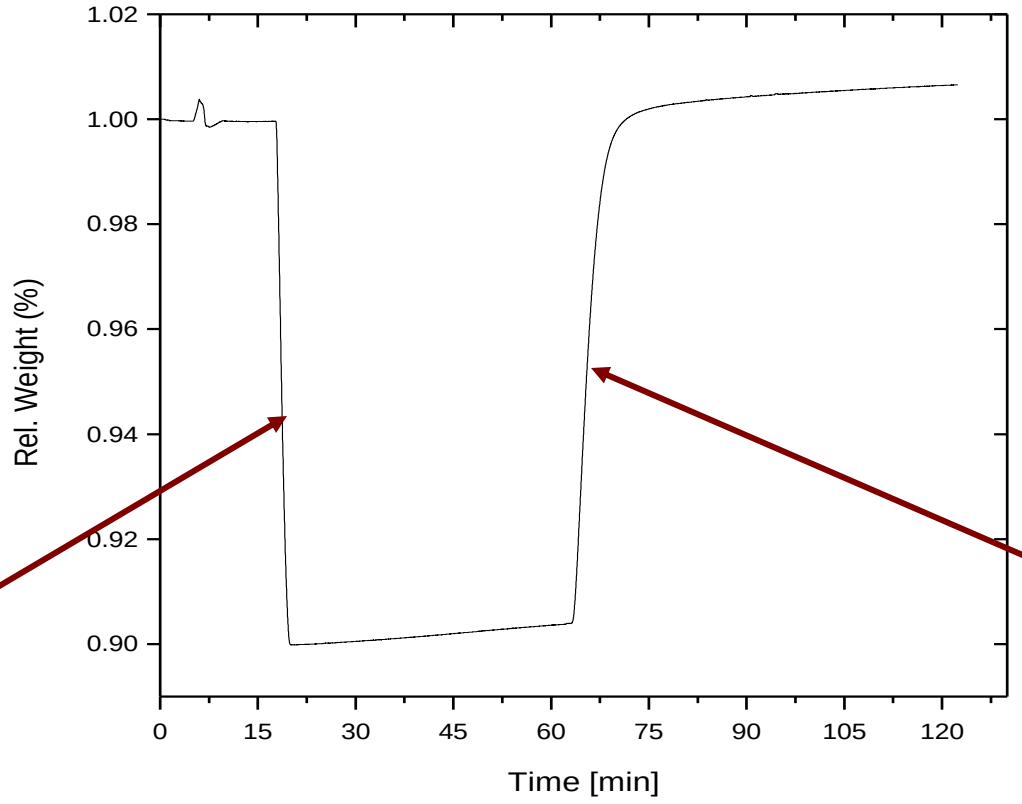
Isothermal 850°C (one cycle: nitrogen for 40 minutes and air for 30 minutes)



CuO decomposition

Cu_2O oxidation

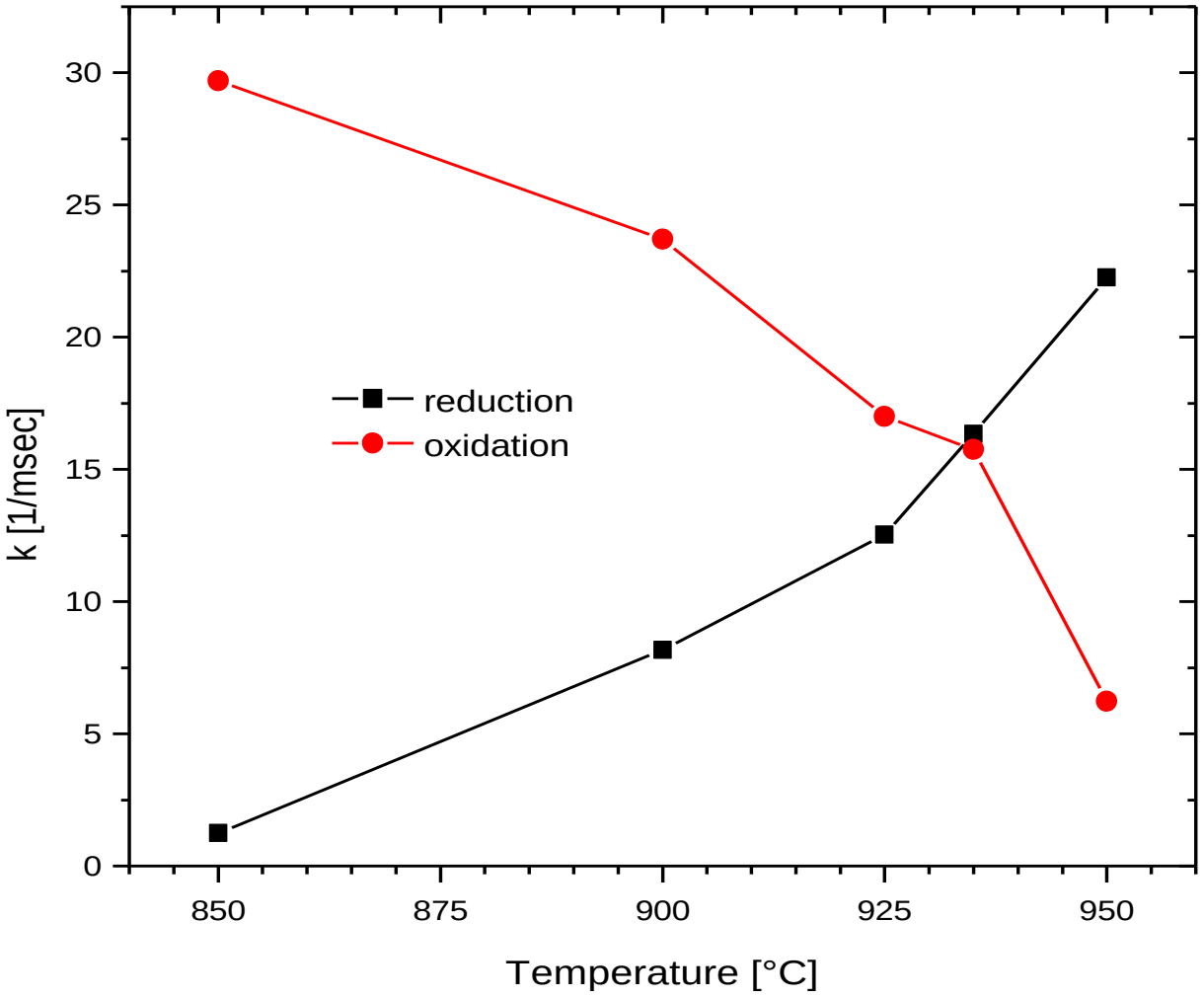
Isothermal 950°C (one cycle between nitrogen 40 minutes and air 30 minutes)



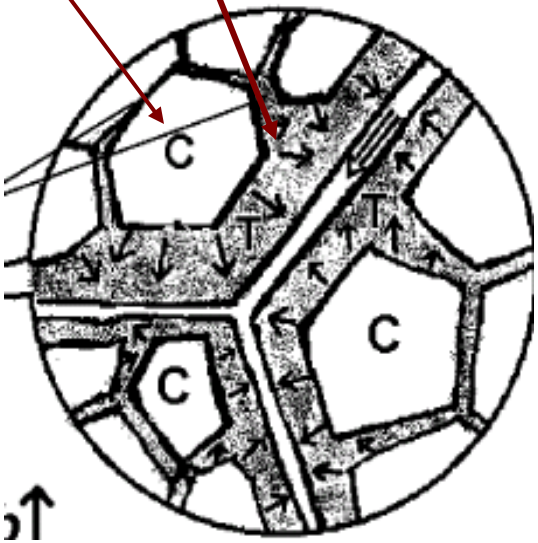
CuO decomposition

Cu_2O oxidation

Fitted first order rate constants for CuO decomposition and Cu_2O oxidation in air



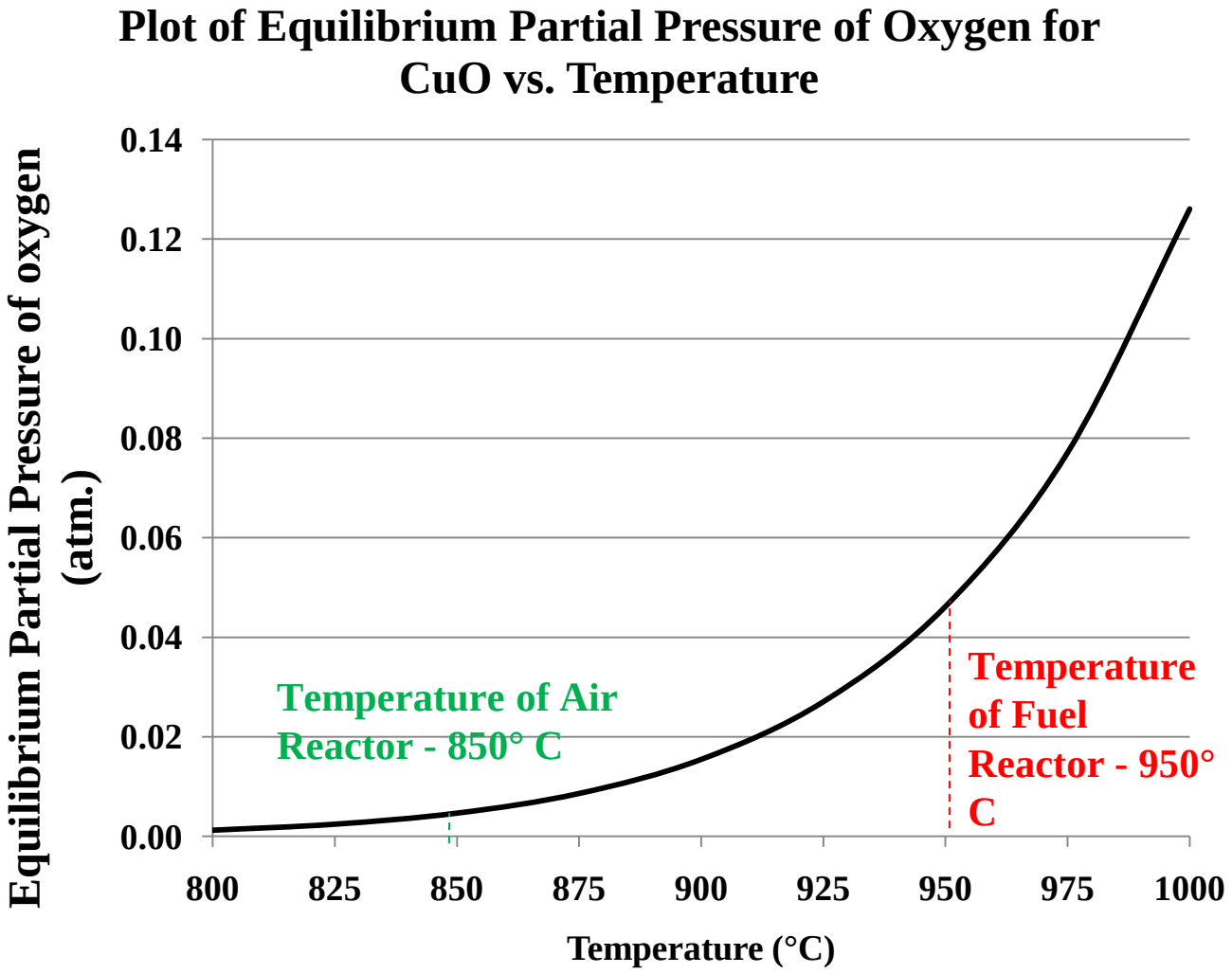
Prisedsky & Vinogradov: Cu_2O grains surrounded by fractured CuO



Zhu, Minura, and Isshiki:

"The activation energy becomes..negative due to sintering of CuO grains" & decrease in grain boundary diffusion

Selection of Temperatures for Air and Fuel Reactors



For air reactor rate is a maximum at ~ 850°C

For fuel reactor rate increases with T but agglomeration is an issue above T ≈ 950°C

Times for CuO/Cu_2O Interconversion

For the preliminary analyses the times were calculated for a plug flow reactor (physically this is approximated by interconnected reactors)

AIR REACTOR

$$\tau_{AR} = \frac{1}{k_{r,Cu_2O}} ln\left[\frac{1 - X_{CuO,FR}}{1 - X_{CuO,AR}}\right]$$

$\tau_{AR} \rightarrow \infty$ when $X_{CuO,AR} \rightarrow 1$

$$\tau_{AR} = \frac{1}{k_{r,Cu_2O}} ln\left[\frac{1}{1 - \left(\frac{\Delta X_S}{(1 - X_{CuO,FR})}\right)}\right]$$

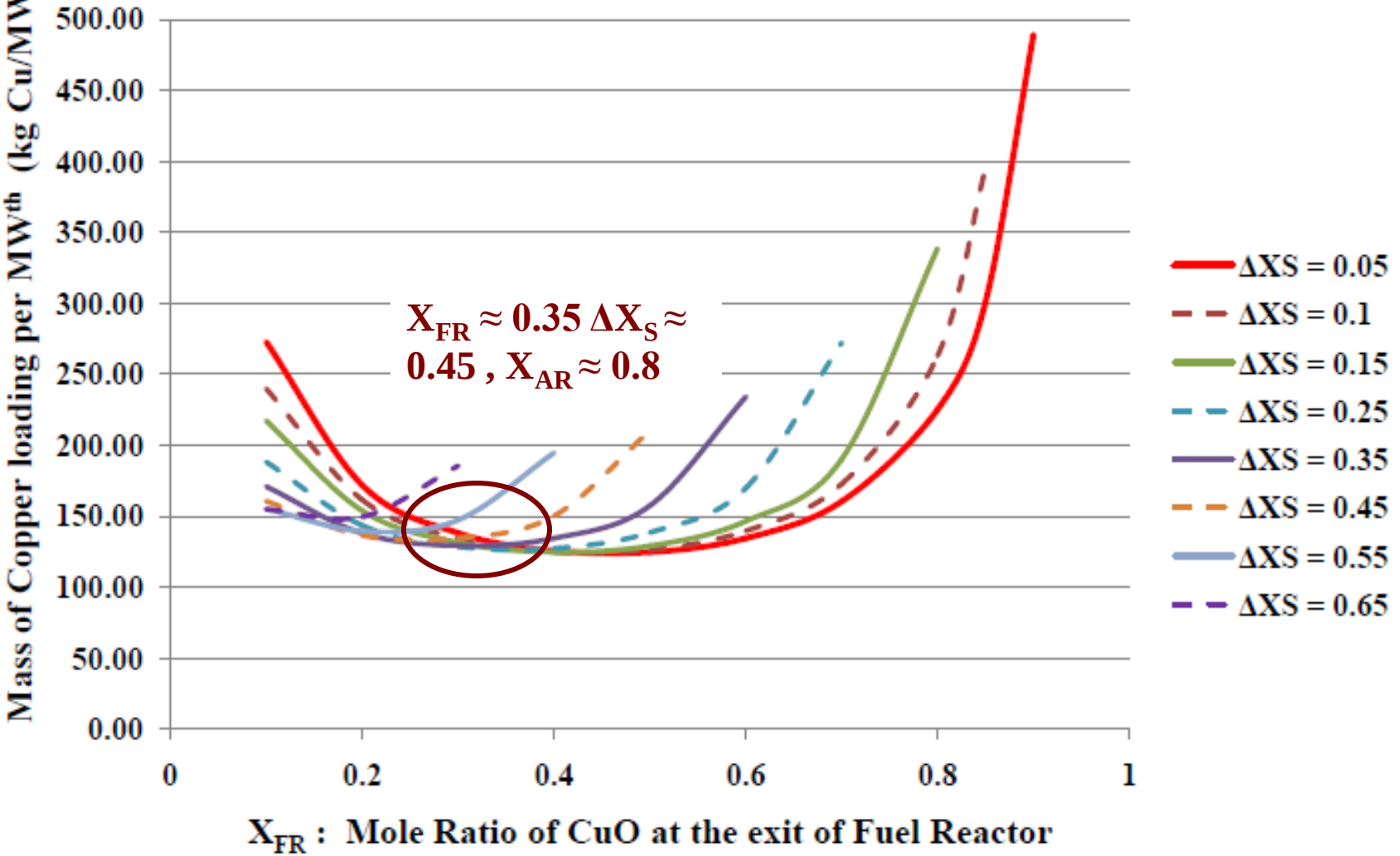
FUEL REACTOR

$$\tau_{FR} = \frac{1}{k_{r,CuO}} ln\left[1 + \frac{\Delta X_S}{X_{CuO,FR}}\right]$$

$\tau_{FR} \rightarrow \infty$ when $X_{CuO,FR} \rightarrow 0$

Mole Loading of Copper in Air and Fuel Reactors $= \dot{N}(\tau_{AR} + \tau_{FR})$

Plot of Mass of Copper loading per MW^{th} vs. Mole Ratio of CuO at the exit of fuel reactor for different ΔX_S (X_{AR}-X_{FR}): PFR Assumption with log mean O_2 concentration



Comparison with Oxygen Carrier Loadings Reported in Literature

Process	OC Loading
CLOU (Utah) with C as fuel	135 kg CuO/MW_t
CLC (CSIC, Sp.) with methane as fuel	25 kg CuO/MW_t
CLC (Chalmers, SE) with coke as fuel	1200 kg Fe_2O_3/MW_t

Carbon concentration in the fuel reactor is determined by equating the rate of oxygen release by CuO to the rate of consumption by carbon

Rate of O_2 generation in the fuel reactor

The rate of reaction $4CuO \rightarrow 2Cu_2O + O_2$ is described by the expression

$$r_{O_2,CuO} = \frac{k_{r,CuO}[CuO]}{4} - \frac{k_{r,Cu_2O}[Cu_2O]p_{O_2}^{1/2}}{2}$$

At equilibrium: $$p_{O_2} = \left(\frac{k_{r,CuO}}{k_{r,Cu_2O}}\right)^2$$

Limiting Cases for calculating O_2 production by CuO decomposition:

$p_{O_2} \rightarrow p_{O_{2,ea}}$ and rate is mass transferred controlled

$$\dot{N}_{O_2,CuO} = k_{m,CuO}A_{CuO}\left(\frac{p_{O_{2,e}}}{RT} - \frac{p_{O_{2,b}}}{RT}\right)\left(\left(\frac{\sigma_{P,CuO}}{V_R}\right)V_R\right)$$

$p_{O_2} \rightarrow 0$

$$\dot{N}_{O_2,CuO} = \frac{k_{r,CuO}[CuO]}{4}V_R$$

Calculation of Carbon Burnout

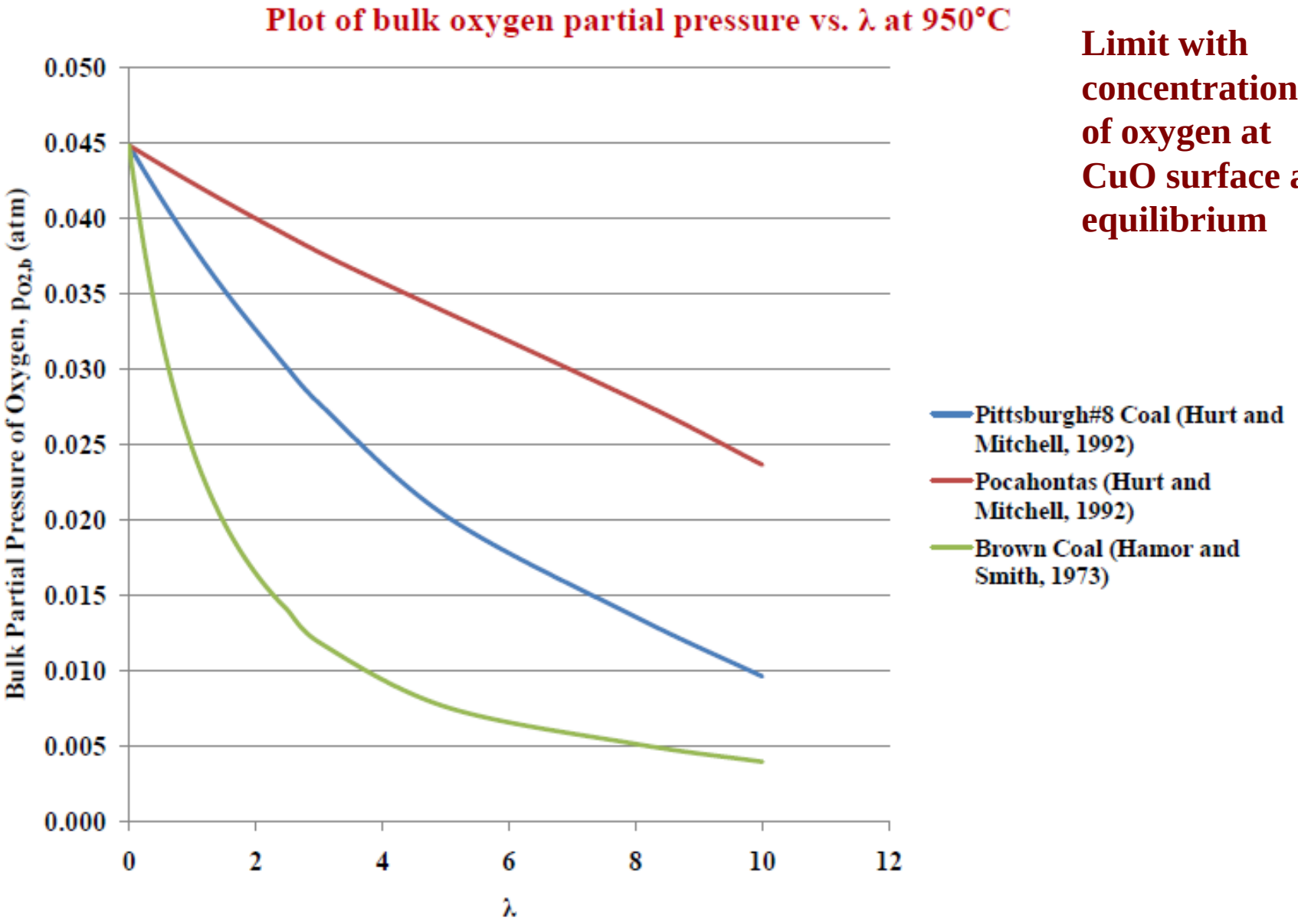
1. Solution for the surface carbon concentration $p_{O_2,s}$ as a function of the bulk oxygen concentration $p_{O_2,b}$ using the expression for surface oxidation of Hurt and Mitchell yields

$$k_{m,C}A_C((mw_C))\left(\frac{p_{O_{2,b}}}{RT}-\frac{p_{O_{2,s}}}{RT}\right)=k_{r,C}A_C{p_{O_{2,s}}}^{\frac{1}{2}}$$

2. The bulk oxygen concentration $p_{O_2,b}$ can be solved from equating the rate of oxygen generation by the decomposition of CuO to that consumed by the carbon. The concentration is a function of the groups representing the ratio of product of mass transfer coefficient and surface areas of carbon and copper oxide and the rate of surface oxidation to the mass transfer coefficient for the carbon particles

$$\lambda=\left(\frac{k_{m,C}A_C}{k_{m,CuO}A_{CuO}}\right)\left[\frac{\left(\frac{\sigma_{P,C}}{V_R}\right)}{\left(\frac{\sigma_{P,CuO}}{V_R}\right)}\right] \quad \text{and} \quad \left(\frac{k_{r,C}RT}{k_{m,C}(MW_C)}\right)$$

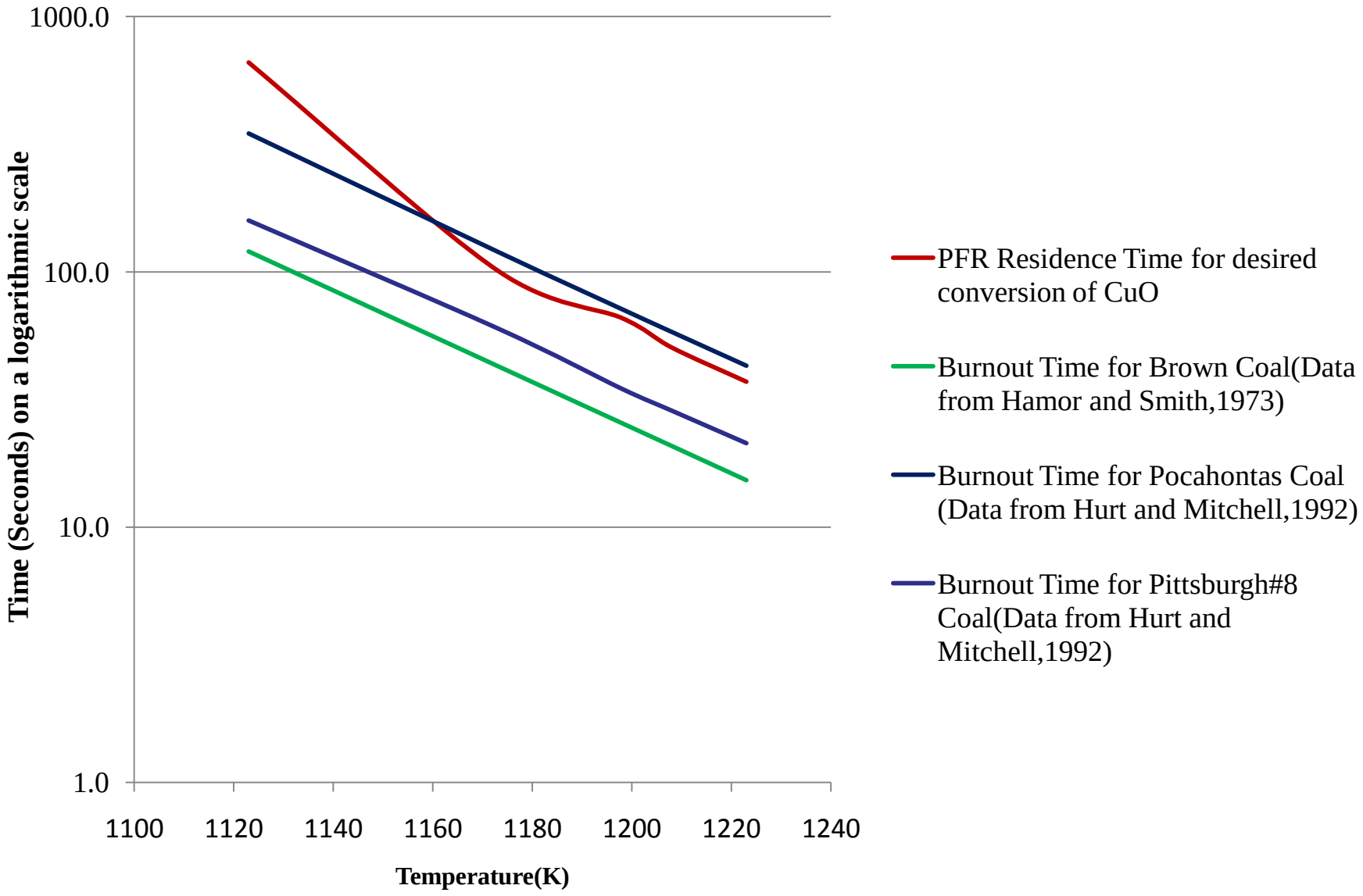
3. The carbon burnout is then calculated using a shrinking sphere model, with due allowance for changes in the governing parameters with time.



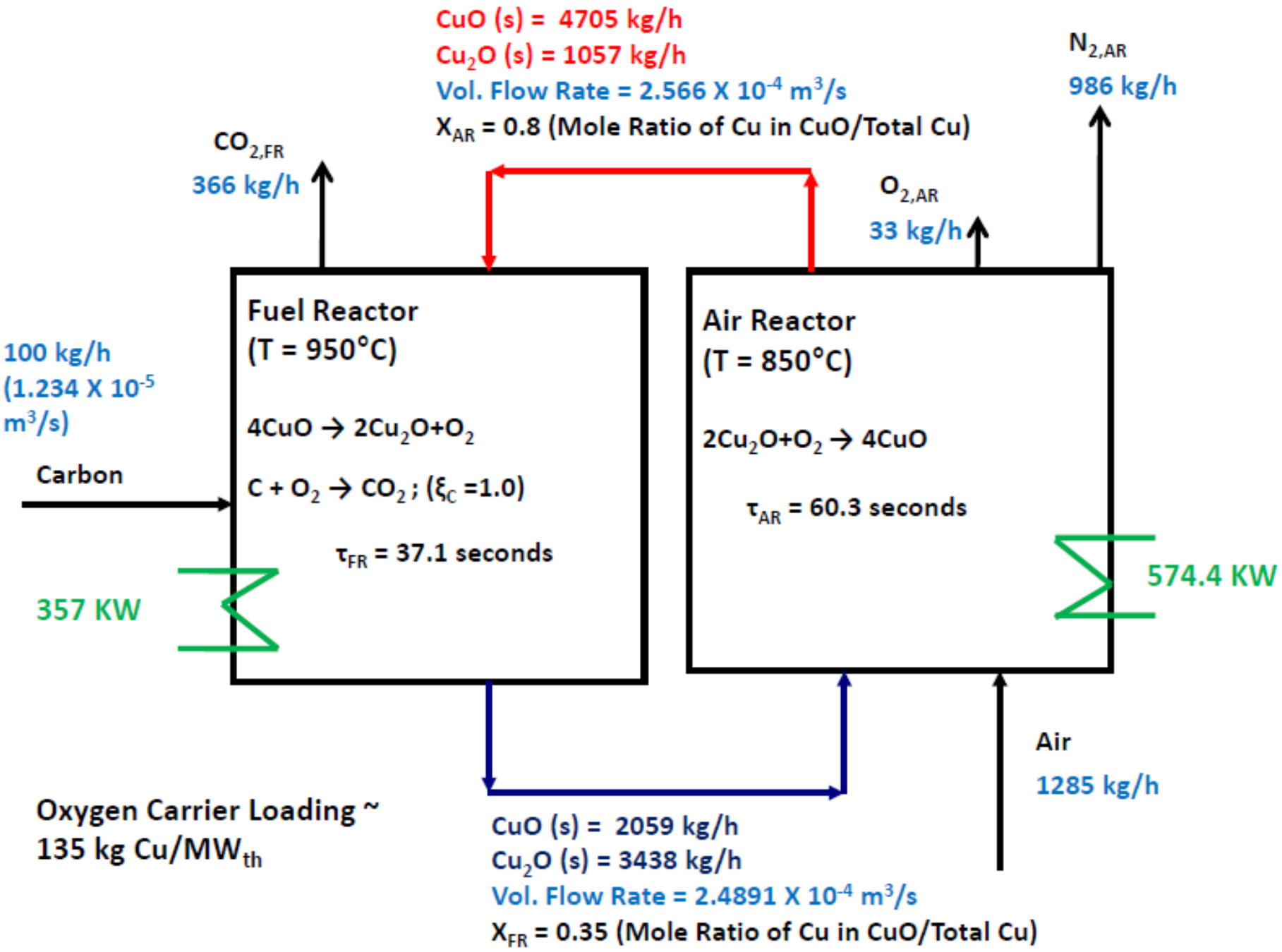
Limit with concentration of oxygen at CuO surface at equilibrium

$$\lambda = \left(\frac{k_{m,C}A_C}{k_{m,CuO}A_{CuO}}\right)\left[\frac{\left(\frac{\sigma_{P,C}}{V_R}\right)}{\left(\frac{\sigma_{P,CuO}}{V_R}\right)}\right]$$

Residence Time for Conversion of CuO > burnout time for coal. This will lead to complete combustion. For periods where time is slightly smaller carbon burnout > 99%.



ASPEN Model of Air And Fuel Reactors


CuO (s) = 4705 kg/h
Cu2O (s) = 1057 kg/h
Vol. Flow Rate = 2.566 X 10-4 m3/s
XAR = 0.8 (Mole Ratio of Cu in CuO/Total Cu)
CO2,FR
366 kg/h
N2,AR
986 kg/h
O2,AR
33 kg/h
Fuel Reactor
(T = 950°C)
4CuO → 2Cu2O+O2
C + O2 → CO2 ; (ξC =1.0)
τFR = 37.1 seconds
Air Reactor
(T = 850°C)
2Cu2O+O2 → 4CuO
τAR = 60.3 seconds
100 kg/h
(1.234 X 10-5
m3/s)
Carbon
357 KW
574.4 KW
Air
1285 kg/h
Oxygen Carrier Loading ~
135 kg Cu/MWth
CuO (s) = 2059 kg/h
Cu2O (s) = 3438 kg/h
Vol. Flow Rate = 2.4891 X 10-4 m3/s
XFR = 0.35 (Mole Ratio of Cu in CuO/Total Cu)

Concluding Comments

- **Advantages of CLOU**
  - **Low carrier loadings (with associated reductions in reactor sizes) because of high rates of char gasification with oxygen (~ 60 fold greater than for CLC).**
  - **Oxygen carrier circulation rate is independent of thermal balance and is low relative to systems where carrier circulation must provide energy to endothermic fuel reactor.**
  - **Flexibility in selecting temperatures of both fuel and air reactors because of exothermicity of both.**
  - **Sulfur contamination not a problem: S is released as SO_2. $CuSO_4$ is unstable (decomposes above 650°C)**
  - **As with CLC, low inherent energy penalty since ASU is eliminated.**
- **Future Studies**
  - **Future studies will address**
    - **issues of OC support, contamination, attrition, sintering in a laboratory fluidized bed reactor (Prof. Whitty)**
    - **optimum reactor configuration and operation**
    - **CFD simulation to evaluate system design (Profs. Smith & Thurnock)**

Acknowledgments

Special thanks are due to our Program Manager, David Lang.

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